Scientific Research Publishing

Advances in Chemical Engineering and Science, 2017, 7, 228-234
http://www.scirp.org/journal/aces
ISSN Online: 2160-0406
ISSN Print: 2160-0392

Synthesis of Crystallized $BaWO_4$ Nanorods in a Microemulsion System

Jie Zhang[1,2], Xiaoshu Zhu[1,2], Heyong Huang[1,2], Yinping Zhang[1,2*]

[1]Nanjing Normal University Center for Analysis and Testing, Nanjing, China
[2]Biomedical Materials Testing Service Center in Jiangsu Province, Nanjing, China
Email: *zhangyinpingnjnu@163.com

How to cite this paper: Zhang, J., Zhu, X.S., Huang, H.Y. and Zhang, Y.P. (2017) Synthesis of Crystallized $BaWO_4$ Nanorods in a Microemulsion System. *Advances in Chemical Engineering and Science*, **7**, 228-234.
https://doi.org/10.4236/aces.2017.72017

Received: February 24, 2017
Accepted: April 25, 2017
Published: April 30, 2017

Abstract

$BaWO_4$ nanorods have been successfully synthesized in w/o microemulsion system containing barium ions via a simple reaction between Ba^{2+} and WO_4^{2-}. The $BaWO_4$ Nanorods were characterized by XRD, TEM, and SEM, respectively. Results showed that the solvents composition—volume ratio of 4-dioxane and distilled water—played the key role in the formation of $BaWO_4$ Nanorods. Furthermore, the strong vibration at 925 cm^{-1} on its Raman spectrum indicated that the $BaWO_4$ nanorods is good at stimulating Raman scattering in transient and steady-state, making it as a promising candidate material for laser with self-raman conversion of radiation inside the active medium.

Keywords

$BaWO_4$ Nanorods, Microemulsion, 4-Dioxane, Raman Spectrum

1. Introduction

Nowadays, tungstate materials, $BaSO_4$, have attracted much attention in view of its luminescent behavior and structural properties [1] [2]. As compared to other materials, the narrow line width of its stimulated Raman scattering (SRS)-active mode in $BaSO_4$ crystal (1.6 cm^{-1}) leads to high peak intensity (63%). In particular, Raman gain has been measured to be 8.5 cm/GW at 1.06 μm wavelength [2]. Furthermore, the material is not hydroscopic and transparent in visible and near-infrared spectral range. It is a promising material for crystalline nano- and picoseconds Raman lasers. A number of methods, including hydrothermal method, flux method and solid-state reaction [3]-[8], have been developed to generate tungstate materials. However, tough reaction conditions, such as high-reaction temperature, long-reaction time or complex equipment, were applied in most this approaches [9]. Thus, seeking efficient but low-cost techniques for synthesizing $BaSO_4$ is required for the development of electro-optical materials.

It is well known that different surfactants can form micelles with variable morphologies. This can be utilized for the modification of crystal growth [10] [11] [12]. For example, Zhang *et al.* [12] reported that the penniform super structures of $BaWO_4$ nanowires have been successfully synthesized in reverse micelles by using a block copolymer as the directing agent. The effects of the mixing ratio between the anionic and cationic surfactants on the crystal growth of $BaWO_4$ nanowires have been further studied. As proposed, the different morphologies and sizes of $BaWO_4$ crystals could be synthesized by the employment of super-molecule templates composed of biomembrane and organic reagents at room temperature [13]. However, the $BaWO_4$ nanoparticles with high crystalline and various regular shapes are required in order to enhance physiccal properties. It has thus been indicated that the $BaWO_4$ microparticles with well crystallinity should be obtained through simple method. Whereas, the composition of the microemulsion influences the structures of the surfactant aggregation as well as the size and shape of the final nanocrystals [14] [15].

Therefore, the present study was conceived to develop $BaWO_4$ nanoparticles in a water-in-oil (W/O) microemulsion system composed of 1,4-dioxane and water. The phases, morphologies, and luminescent properties have been investigated.

2. Experimental Section

$BaCl_2 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ with analytical grade purity were used as, and all other chemical reagents were analytical grade. $BaWO_4$ nanoparticles were obtained from $BaCl_2$ and Na_2WO_4 microemulsion system according to the following reaction:

$$BaCl_2 + Na_2WO_4 = BaWO_4 \downarrow + 2NaCl$$

Firstly, 4-dioxane and distilled water were mixed together to prepare a microemulsion system with different volume ratios. Secondly, $BaCl_2 \cdot 2H_2O$ (0.061 g) and $Na_2WO_4 \cdot 2H_2O$ (0.0821 g) were dissolved in an aliquot of 10 mL of microemulsion system, respectively. The mixture containing Na_2WO_4 were then added dropwise into the flask containing $BaCl_2$ at 35˚C and 150 rpm. After mixing for 10 min, the sample was centrifuged at 4024 ×g for 5 min and the white precipitates were collected. Finally, the white precipitates were rinsed three times with distilled water and dried at 80˚C for 6 h.

The X-ray diffraction (XRD) patterns were recorded using a Janpan Ridaku D/Max-γA X-ray diffractometer. The particles size and morphology were characterized by scanning electron microscopy (SEM, JEM-200CX) and transmission electron microscopy (TEM, JEOL-2010). Raman spectra were measured at the 514.5 nm line of an Ar laser (Labram HR800).

3. Results and Discussion

The obtained $BaWO_4$ particle in water-in-oil (W/O) microemulsion system was characterized by XRD, and the typical XRD pattern was shown in **Figure 1**, in which all the peaks could be indexed to the pure $BaWO_4$ particle with a tetragonal unit cell (a = b = 0.5626 nm, c = 1.2744 nm). This can be indexed to the JCPDS Card No. 82,457 [12]. No other peaks were detected in the pattern, indicating the high purity of the $BaWO_4$ particle.

The typical TEM images of products synthesized with different ratio of 4-dioxane and distilled water were displayed in **Figure 2**. **Figure 2(a)** showed that $BaWO_4$ particles with large side length were developed without the addition of 4-dioxane.Whereas, as can be seen from **Figure 2(b)** and **Figure 2(c)**, with an increase of the ratio of 4-dioxane and distilled water from 3:7 to 5:5, the diameter of produced rods significantly reduced from 500 nm to 30 nm. Finally, as indicated from **Figure 2(d)**, when the ratio value reached 6:4, it totally transformed from rods to fine spherical particles. These images implied that the concentration of 4-dioxane played a crucial role in the formation of $BaWO_4$ nanorods. Generally, the formation of $BaWO_4$ crystal basically consists of a nucleation step followed by particle growth stages: In the initial stage, some of nuclei were formed. However, in the particle growth stages, the development of the crystallite is controlled by 4-dioxane. 4-dioxane is also considered as a stabilizer preventing the aggregation during the formation of nanocrystals. Thus, no special morphologies would form in the single aqueous system in the absence of 4-dioxane because no formation of templates for the preparation of $BaWO_4$ nanorods. It is well known that different concentrations of surfactants can form micelles with varied morphologies [15], which could be utilized for the modification of crystal growth. Nevertheless, higher concentration of 4-dioxane on $BaWO_4$ crystals resulted in an isotropic growth mode and nearly equiaxial particles, which unfavored the formation of $BaWO_4$ nanorods. Similar results have also been reported by other groups [14] [16] [17]. Additionally, the TEM and

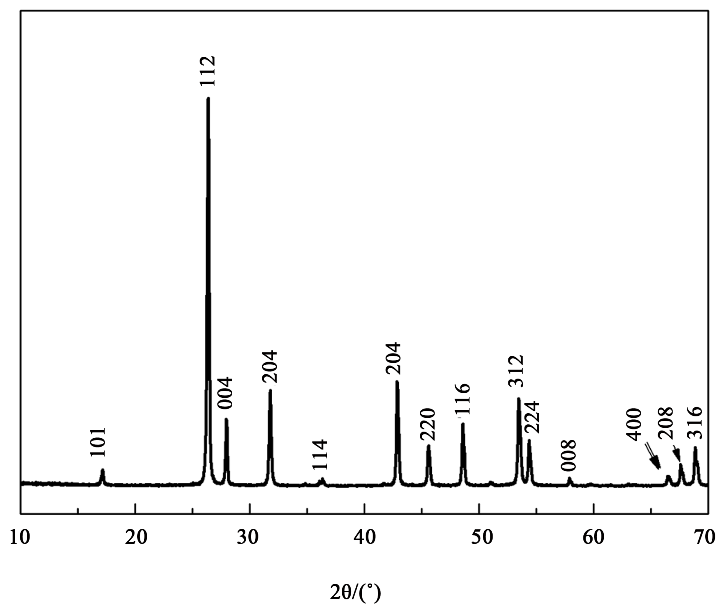


Figure 1. XRD patterns of $BaWO_4$ Nanorods.

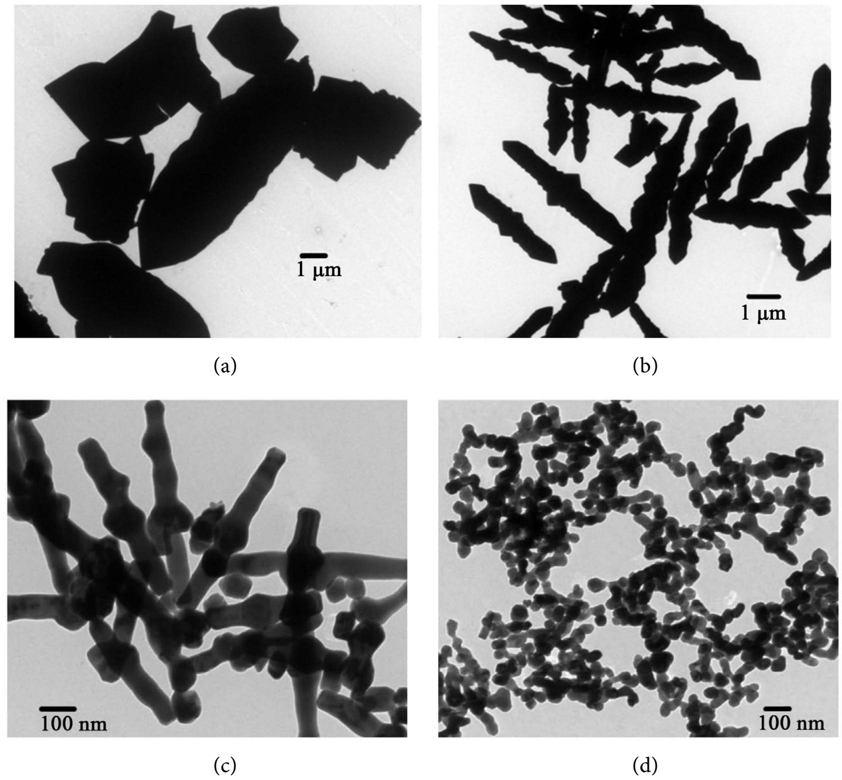


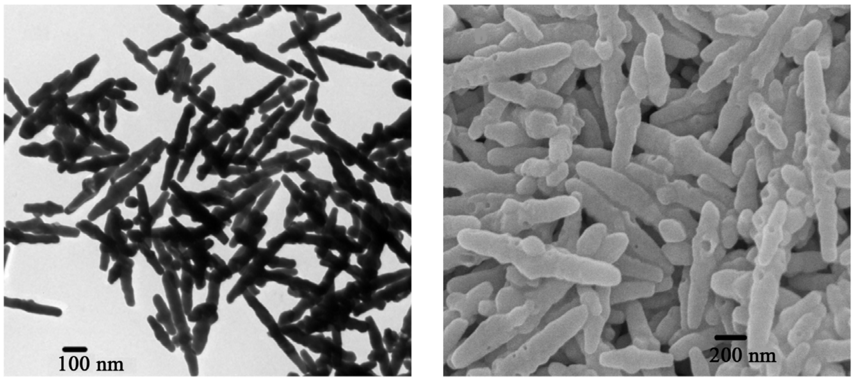
Figure 2. TEM images of the produced $BaWO_4$ with different ratio of 1,4-dioxane and water. (a) 0:100; (b) 2:8; (c) 5:5; (d) 6:4.

SEM image of $BaWO_4$ nanorods prepared in the solvents with the ration value of 4:6, was showed in Figure 3. The side length was approximately 600 nm, and the diameter was about 50 nm.

The Raman spectra of the produced $BaWO_4$ nanorods with a ration value of 4:6 was shown in Figure 4(a). The peaks at 926.5, 830.7, 794.6 and 330.6 cm^{-1} belongs to vibration mode of ν_1 (A_g), ν_3 (B_g), ν_3 (E_g) and ν_2 (A_g), respectively. Furthermore, a strong vibration at 925 cm^{-1} was observed, indicating the $BaWO_4$ nanorods is good at stimulating Raman scattering in transient and steady-state [2]. This made it as a promising material for laser with self-raman conversion of radiation inside the active medium. The blue emission from $BaWO_4$ materials has been reported at low temperatures in the literature [18] [19] [20]. Interestingly, as shown in Figure 4(b), a broad emission band extended from 396 nm to 498 nm (peaked at approximately 425 nm) was observed when the $BaWO_4$ nanorods excited at 270 nm. The blue emission from $BaWO_4$ nanorods is known to be due to radiative transitions within $\left(WO_4^{2-}\right)$ molecular complexes. Hence, a similar mechanism for tungstate materials has been reported in the literature [8] [21] [22] [23].

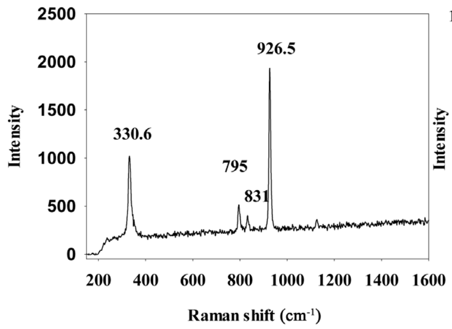
4. Conclusion

In the present study, $BaWO_4$ nanoparticles have been prepared in water-in-oil (W/O) microemulsion systems composed of 1,4-dioxane and water with varied volume ratios. The results of typical TEM images indicated that the concentra-



(a) (b)

Figure 3. The TEM (a) and SEM (b) images of the produced $BaWO_4$ with a ratio of 1,4-dioxane and water for 4:6.



(a) (b)

Figure 4. The Raman spectra of produced $BaWO_4$ nanorods with a ration value of 1,4-dioxane and water for 4:6 (a), and its emission spectra at an excitation wavelength of 270 nm (b).

tion of 4-dioxane played a crucial role in the formation of $BaWO_4$ nanorods with different morphologies. Thus, the addition of 1,4-dioxane should be controlled. Furthermore, the Raman spectra of the produced $BaWO_4$ nanorods indicated that it is a promising material for laser with self-raman conversion of radiation inside the active medium.

Acknowledgements

This work was financially supported by the Natural Science Foundation of Jiangsu Province (13KJB150023, 15KJB210003, BK20150976), and the Natural Science Foundation of China (41501239).

Highlights

$BaWO_4$ nanorods have been successfully synthesized.
The ratio of 4-dioxane and water played the key role.
The bands of produced $BaWO_4$ nanorods vibrated strongly at 925 cm^{-1}.

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